A New Model for the Structure of Silica Glass

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Abstract

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Introduction

The structural description of glasses, and that of silica glass in particular has attracted the attention of scientists for many years. The major problem experimentally is that since the material is not made up of unit cells which repeat in all three directions, diffraction studies of the usual single-crystal type may not be used to explore the details of the atomic structure. Methods which are much less definitive, provide results which are often open to interpretation. In this paper we will present a new model for silica glass, which, like the others is at present untestable experimentally in a direct way, but is one which is compatible in qualitative terms with the observations which have been made.

First we very briefly review existing models of silica glass. In general terms there are three. The first model to be published was that of Zachariasen [1], who envisaged a continuous random network of vertex linked silicate tetrahedra. In his model, very much akin to that of a condensed gas, there are a whole range of bond angles and dihedral angles associated with $-Si-O-Si-O$ rings of various sizes. Phillips did not like the random nature of the Zachariasen scheme and his model [2,3,4,5] proposed pieces of microcrystals packed together in the glass in random orientations. The trouble with this idea is that a little model-building shows that there are frequent poor contacts between the units so that 'dangling bonds' either force a surface reconstruction or just hang unattached. The third model, the paracrystal model of Hosemann [6] suggests that really silica glass consists of a material with the connectivity of one of the SiO_2 polymorphs, such as cristobalite but where the atoms have been randomly moved by a small distance away from their equilibrium positions, a viewpoint close to that of the situation in one type of metamic state. The new model, which we call the modulated network model is in fact a marriage of the continuous random network model and the micro-crystalline model. It makes use of characteristic structural features found in crystals of the SiO_2 polymorphs and recognizes the importance in both silica and silicate chemistry of the very soft $Si-O-Si$ bending motion [7,8] around an 'equilibrium' value of 145^0. The model also produces a network of completely bonded silicate tetrahedra and thus no dangling bonds. Our arguments in this paper will be geometrical ones, and, as such, will be associated with all the disadvantages which face authors who try to describe a structure in words and pictures printed on a two-dimensional page. We shall therefore first describe our model briefly and then justify various aspects of it by using results from model building and theorems from geometry and topology. The mathematical results are reserved for the appendix. This work is a direct continuation of the work of Marians on the structure of silica networks [9,10,11,12,13,14].

The Model

Our aim is to provide as much detail as possible concerning the structure of a glass where each silicon and oxygen atom is fully chemically bonded. The starting point of the model lies with the characterization of a fully bonded, infinite silica network (Figure 1) whose irreducible rings are 6-rings (Definitions of terms such as these are given in the Appendix).

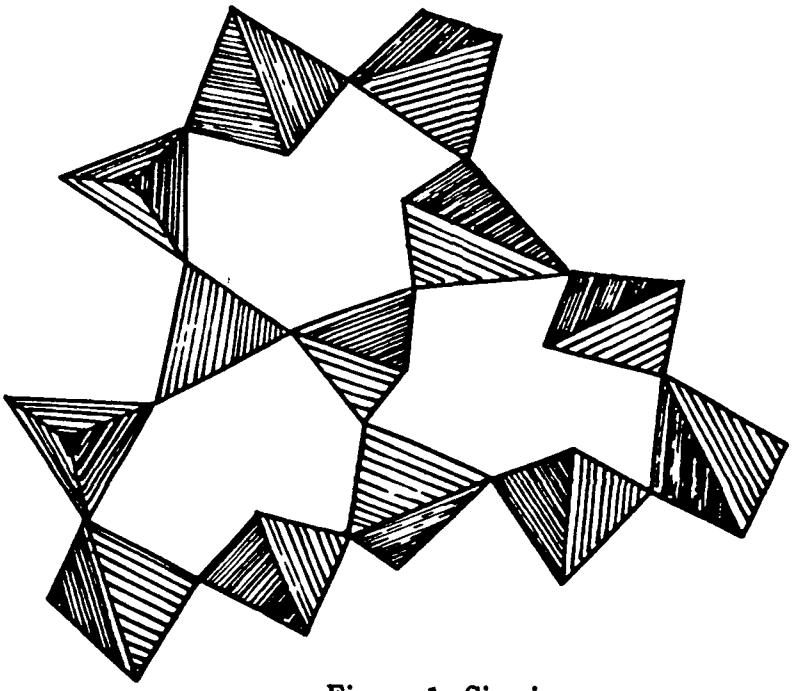

Figure 1: Six-rings

Both cristobalite and tridymite, two high temperature silica polymorphs contain such rings. They differ only in the stacking sequence of sheets of tetrahedra, ABC for (cubic) cristobalite and AB for (hexagonal) tridymite. Importantly the linkages between the sheets in these dimorphs are made using 6-rings. We show later that the only way to put together adjacent sheets is either in a cubic or hexagonal way so that any pattern of stacked sheets can be described by a symbol such as *hhcchc* and a unique direction along which these tridymite-like and cristobalite-like layers are stacked.

Such a silica-network, fully bonded and composed entirely of indecomposable 6-rings would be a one-dimensional crystal. (We define later our topological use of the word indecomposable.) It would give a discrete, if somewhat noisy, diffraction picture for any orientation perpendicular to the preferred direction, but would not be a glass. We note then the important result that a silica network whose irreducible rings are predominantly 6-rings thus must owe its glassy nature to the presence of either point defects or rings other than 6-rings.

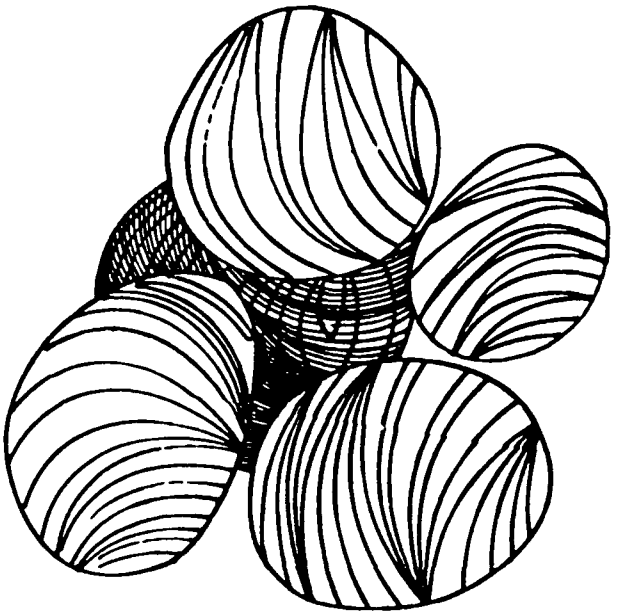

Figure 2: Regular domains in glassy silica

One of the building blocks of our model is a finite (in all three dimensions) piece of such a one-dimensional crystal which is a convex domain (called that because any line segment which has its vertices in the domain is contained entirely within it). At its simplest our model comprises such domains which are 'almost' crystalline in one-dimension, glued together by less ordered interfacial material which contains a larger variety of ring sizes, some smaller rings but mostly 8- and larger rings. The arrangement of domains and interfacial material can be envisaged as in Figures 2,3. Each such domain, except for its boundary layer (probably two tetrahedra thick as we suggest later) is a one-dimensional network-crystal. Taken together these domains contain the bulk of the 6-rings of the network. The vector which defines the stacking direction of the sheets in a particular domain need not be parallel to those describing other domains.

Another way of generating a special case of the geometrical result of our model is to take a crystalline material of the cristobalite or tridymite type and simultaneously distort and rotate regular regions of the crystal while rearranging the connectivity of the atoms in the material which will form the interfacial regions. There will not be enough tetrahedra in the interfacial regions to fulfill the function of this part of the glass (as we will see later) so more must be supplied. Another result of the construction is that the convex domains will be much too regular, all having the same stacking pattern since we started off with a single polymorph. Such a relationship is however useful, since it allows geometrical connections to be made between the glass and crystal.

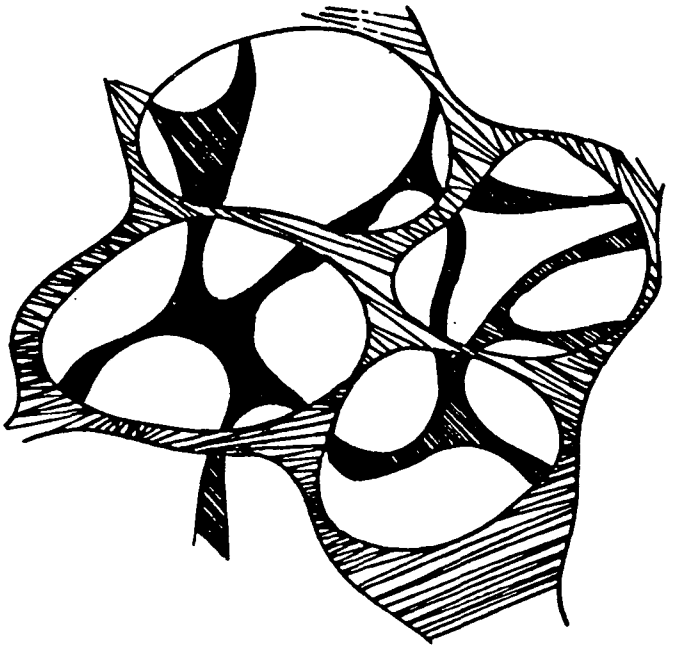

Figure 3: Interfacial material in glassy silica

Our model may then be viewed as a marriage of the continuous random network model of Zachariasen [1] and the micro-crystalline model favored by J. C. Phillips [2,3,4,5] among others. Within the tradition of the continuous random network model no grain boundaries or regions of condensed point defects are either assumed or necessary to the understanding of the structure. Within the tradition of the micro-crystalline model the structure is non-uniform. Fluctuations in network structure are an important aspect of our model and presumably physical properties will fluctuate too. The model is an extension of the continuous random network model in giving a detailed specification of the structure of the network and we can extend the micro-crystalline model by giving a rationale for both the scale of the modulation in network properties and a description of the network structure of the interfacial region. This description of the interfacial region does not require the presence of point defects (i.e. dangling bonds). Our model postulates a nearly continuous variation of properties, and a continuous transformation, between the bulk and the interface as contrasted with the sharp interface between adjacent grains or crystallites proposed by the micro-crystalline model. The model has some aspects of the Hosemann [6] approach too. The coordinates of the atoms in each convex domain are different from what they would be in the crystal, but the connectivity is similar.

The atomic coordinates of the *atoms* in these subnetworks need not be coplanar far less periodic. We expect a domain diameter in the range 1.5nm to 10nm, both bounds being correct within an order of magnitude only. We have built physical models with

domains which when scaled were on the order of 1nm. These models were constructed of plastic tetrahedra held together at the vertices by pipe cleaners. The directional preference of the regular domains would certainly have been seen experimentally with domains as large as 5nm. In that range, the material would diffract as a microcrystalline powder of similar grain size. We also mention that since the curvature of a surface is inversely proportional to its radius, a large domain has an almost flat surface. This would influence the preferred direction of nearby domains, giving the entire ensemblage an orientational coherence. One can imagine very large domains, well oriented which could describe a single (one-dimensional) crystal. Thus the domain size in the glass has to be relatively small; otherwise, these restrictions will tend to encourage crystallinity.

There are several results which come from model building which are difficult (at present we believe impossible) to describe in an analytic way. We find that an irregular domain geometry allows almost regular networks with only 6-rings to be bonded together with minimal interfacial material. Our models invariably had interfacial material comprised of mostly 8-rings. A determinant of the size of these domains is the volume fraction of larger rings and its distribution. Our models had less than one-tenth volume fraction interfacial material. Experience with models is that one 6-ring replaced by 8-rings generates approximately three near-by 8-rings. The eight-membered rings are similar to those shown in Figure 4.

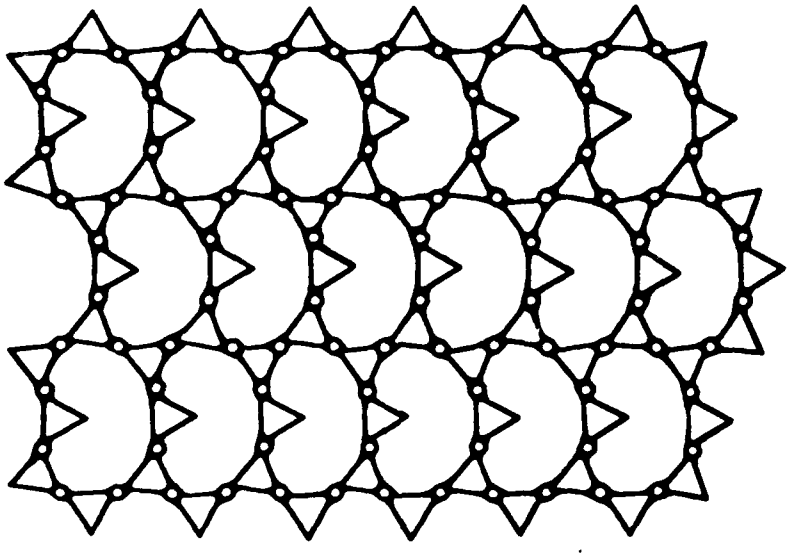

Figure 4: Network of 8-rings as seen in quartz with tetrahedra represented by triangles

The size to which the near-regular domains can grow is limited by the time available

for readjustments as newly attached tetrahedra find a good fit between the conflicting requirements of the differing distortions to ideal angles and bond distances. We envision a process similar to epitaxial growth of one crystal on a crystallographically friendly plane of a similar but different crystal. In this sense kinetic considerations limit growth and influence the distribution of ring-sizes.

In summary then, the domains are nearly-regular one-dimensional crystals a few nanometers in diameter. The interfacial region as shown in Figure 3 is quite thin between the large faces of two adjoining regions, composed of possibly a single 8-ring in places. There are corners or holes, which, when viewed from the point of view of the domains, are regions where the interface bounds several domains, and which look to the interface like the spokes of a wheel. These regions of the interface are not two-dimensional, but are more irregular and less easy to characterize than those of the domains. We are able to say though that such regions contain a large concentration of both larger and, if they occur, smaller rings than those found in the domains, and possibly a greater range of dihedral angles. The domains and interfacial regions differ too in the distribution of bond angles. The domains are evisioned as having a large number of small distortions of dihedral angles, the interfacial region some small number of highly distorted angles. The interfacial region has taken up the accumulated misfit, much as dislocations between misoriented grains or across any interface with a near but unequal matching of lattice planes. If the domains were perfectly crystalline then the interfacial material might have to be almost as extensive as the crystalline domains themselves to allow connections without enormously strained bonds. In this model the bonding between the domains and the interfacial regions is a cooperative affair, strain in the network-crystalline, geometrically non-crystalline domains, balanced by an interfacial region dominated by larger rings.

The remainder of this paper shows how the geometrical aspects of this problem link together. To justify our model we will need to rely on theorems and results from graph theory and geometry. We are limited by two-dimensional representations of three-dimensional objects in this paper and so will start in two dimensions.

Two-Dimensional Silica Glass

Two-dimensional glasses offer a nice introduction to our ideas. A network composed of vertex-connected-triangles, with two triangles meeting at each vertex and where no other intersections are allowed, is the two-dimensional analogue of the network of a silica glass. If the irreducible rings of this network are all 6-rings then the network is a pseudo 6-ring-crystal. Such pseudo-crystals have been studied by Hosemann [6] where he used the term paracrystals. A pseudo-crystal (Figure 5 shows an example) is a distorted crystal. Its unit cell is the whole crystal; only its network is periodic. The two-dimensional model analogous to that of the three dimensional glass described above is shown in Figure 6. It has regular regions as seen in Figure 5 glued together by an interfacial region containing non-6-rings.

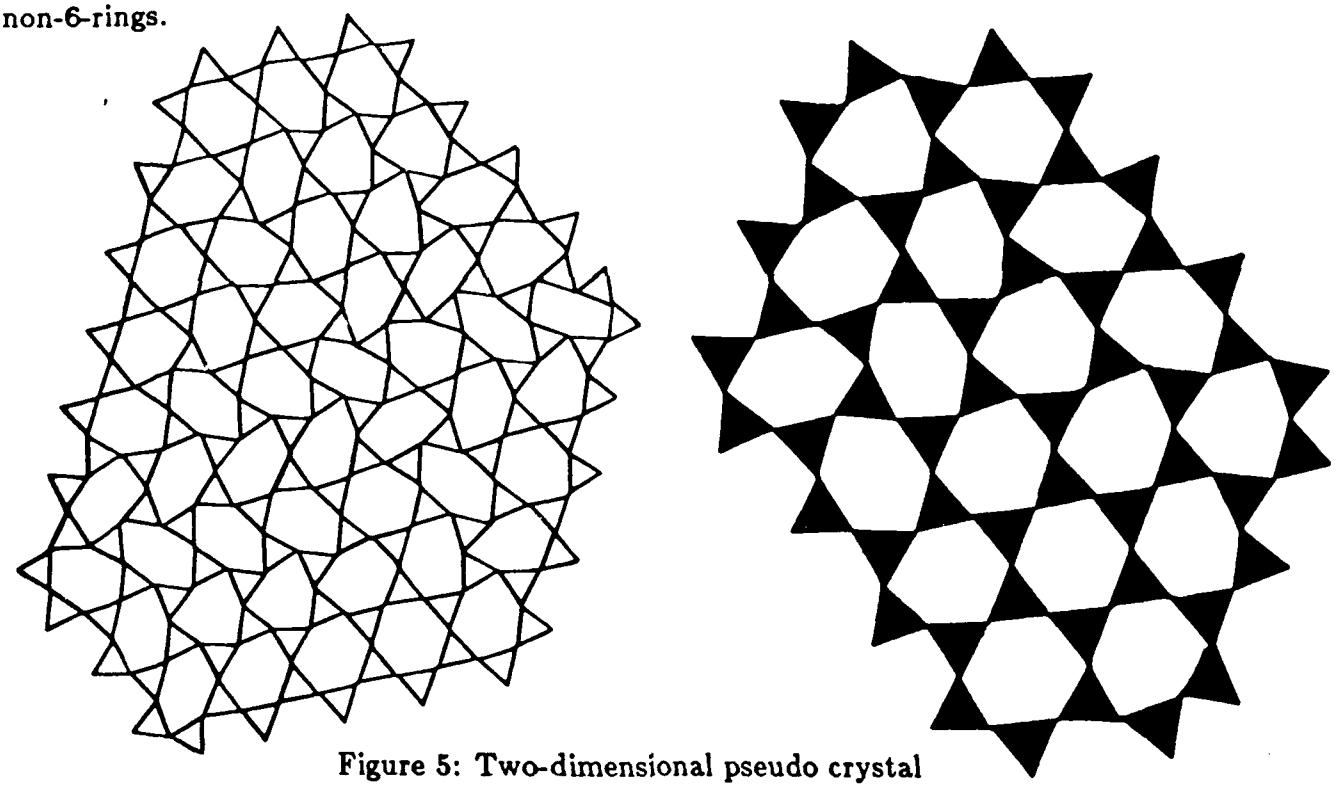

Figure 5: Two-dimensional pseudo crystal

We can see this by assuming the non-6-rings (which we will call defect-rings or defects) to be isolated and sparse in number. We can mark the defect-rings in the network Figure 7 and draw convex domains not containing the defects as in Figure 8. This is the two dimensional analogue of the three-dimensional glass structure described above. Figure 6 looks at first a bit like a continuous random network, but our construction (Figures 7,8) has simply showed it to be composed of convex domains dominated by 6-rings, linked by interfacial material.

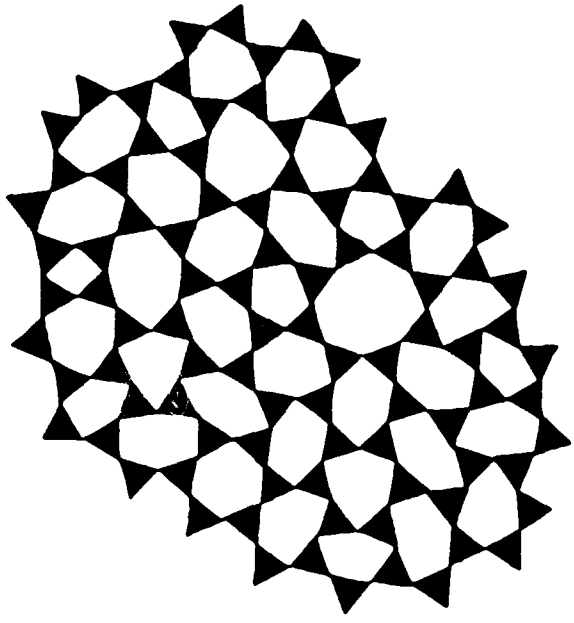

Figure 6: Two-dimensional glass

A two-dimensional triangular network with irreducible 6-rings is a network-crystal as shown by Marians in [14]. (The corresponding result in three dimensions is more complex.) Intuitively this is the statement that there is only one two-dimensional network with only 6-rings. More formally one sees that if there are only 6-rings in a two dimensional network then every triangle has the same local cluster, the one composed of three 6-rings. Two networks with only 6-rings can be made to correspond by picking a triangle from each net and proceeding to extend the correspondence from them to their first, second, etc network-neighbors. This works since each triangle has the same local cluster and there is only one way for next neighbors to connect.

This last result shows that the defect-free domains must be (up to network equivalence) crystalline. Since the average ring size of a two-dimensional three-connected network is six, the boundary layer containing non-6-rings in the two-dimensional glass must contain both larger and smaller rings. We note this as an example of a familiar occurrence, disorder is associated with a broader distribution of ring sizes.

We now study two particular two-dimensional networks as a prelude to our final discussion concerning the three-dimensional structure of silica glass. Recall that the size of a ring is the number of triangles, or tetrahedra, depending on the dimension, which it contains. Thus a six-ring contains twelve atoms, $(SiO)_6$ with the oxygen atoms at the vertices and the silicon atoms at the centers of the triangles.

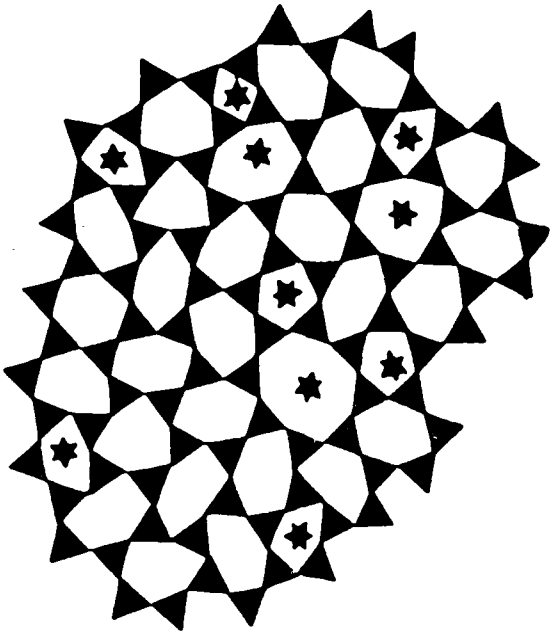

Figure 7: Defects in a two-dimensional triangular network

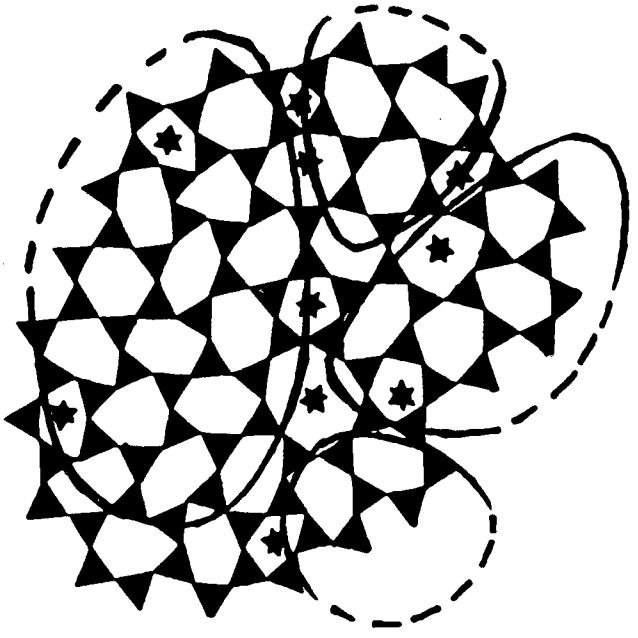

Figure 8: Convex domains in a two-dimensional glass dominated by 6-rings

The first structure is the familiar 3-connected network comprised of 6-rings, known as the honeycomb network and shown in Figure 9. With the nodes of the network representing single atoms, this is the two-dimensional subnetwork of the diamond structure perpendicular to the $[1,1,1]$ direction. With the nodes represented by triangles as shown in Figure 10 the triangular 6-ring-crystal results and if the triangles are now replaced by tetrahedra we have the two-dimensional subnetwork of tridymite perpendicular to the $[0,0,1]$ direction, or of cristobalite perpendicular to the $[1,1,1]$ direction. In this connection note that we replaced the triangles by tetrahedra without any restrictions on the relative positions of the tetrahedra to each other or to the surface containing the triangles. (We refer to a surface rather than a plane here since the triangles need not be in the same plane). The tetrahedra in the basal plane of tridymite and in the $[1,1,1]$ direction of cristobalite alternate pointing up and down as shown in Figure 11. The tetrahedra in a sheet or slab parallel to the c axis in tridymite alternate in pairs Figure 12. In the ideal configuration of tridymite, all of the dihedral angles are 180^0, the network of tetrahedra is bent appropriately between successive pairs of upward or downward pointing tetrahedra to accommodate these angles.

The second structure involves two-dimensional subnetworks composed of 8-rings. First in Figure 13 we show a two-dimensional network of 8-rings which is an irreducible subnetwork of quartz appearing in the $[1,1,2]$ orientation. The network of Figure 13 is reducible as a subnetwork of β-BeO appearing in the $[1,0,1]$ as shown in Figure 14. We note that $\alpha - BeO$ has the wurtzite structure, related by a single atom spacer to that of tridymite. The 6-rings into which the 8-rings decompose are dashed. The orientations given are of necessity approximate, these networks are not planar and as a result do not have a well specified orientation. Recall that a uniform 3-connected network would have average ring size of six. Thus a network with only 8-rings must have some nodes which are not three-connected. Figure 15 shows the derivation of this network from the honeycomb network. The unfilled circles added to the honeycomb network when filled produce the network of 8-rings. Thus importantly for our model of silica glass we may generate a piece of interfacial material from a $[1,1,1]$ slab by simple insertion of extra tetrahedra. Note that there are two-connected sites in such a sheet which allow connections to either side of it. Figure 4 shows this network as it appears in quartz with the approximate orientation $[1,1,2]$; the tetrahedra have been represented as triangles.

Last we consider the network of 8-rings in the $[0,0,1]$ orientation in quartz. Nodes which alternate in 4-connected and 2-connected modes are seen. Additionally note the rotation of 120^0 of successive subnetworks in the c-direction. With the nodes represented by tetrahedra this network is represented schematically as triangles Figure 16, and seen with the nodes represented by circles this network is shown in Figure 17. It is interesting

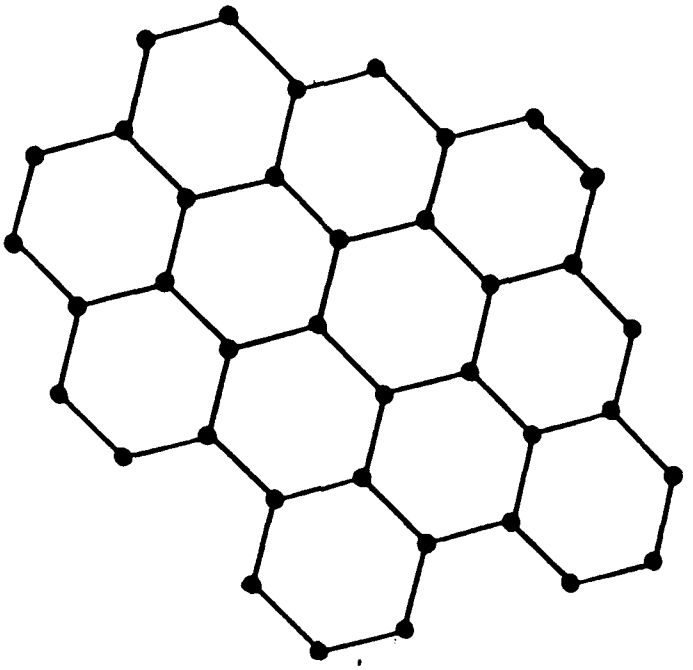

Figure 9: Honeycomb network

at this stage to point out a rather coarse, but illuminating view of our model of silica glass. The convex domains are composed of cristobalite/tridymite-like units while the interfacial region is composed of quartz-like units, in the sense that six-rings are a feature of cristobalite and tridymite and eight-rings a feature of quartz.

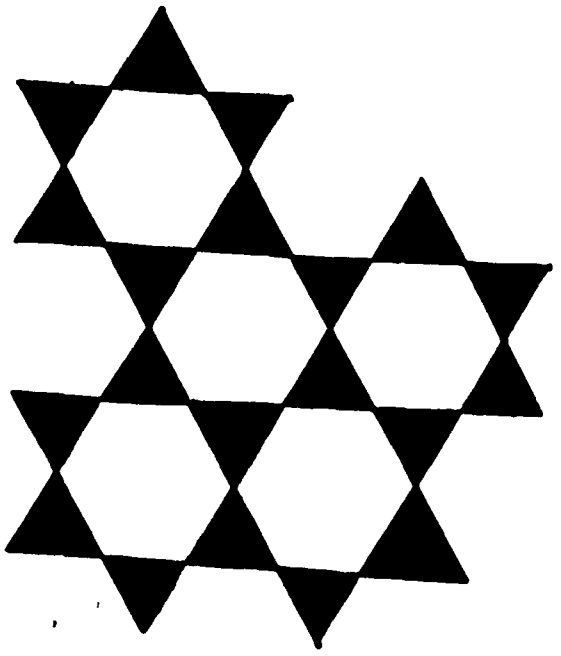

Figure 10: Triangular crystal

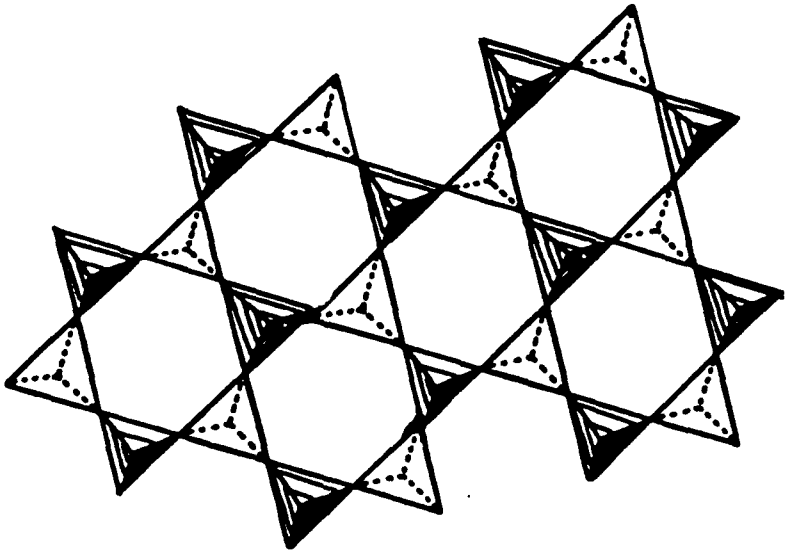

Figure 11: Alternating tetrahedra on triangular network as occurs in basal plane of tridymite and on $[1,1,1]$ plane in cristobalite.

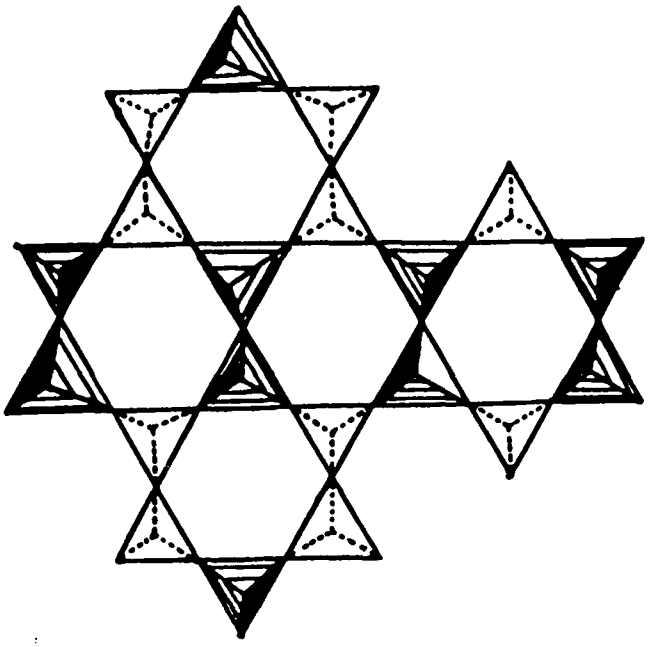

Figure 12: Alternating pairs of tetrahedra on triangular network as occurs parallel to the c axis in tridymite.

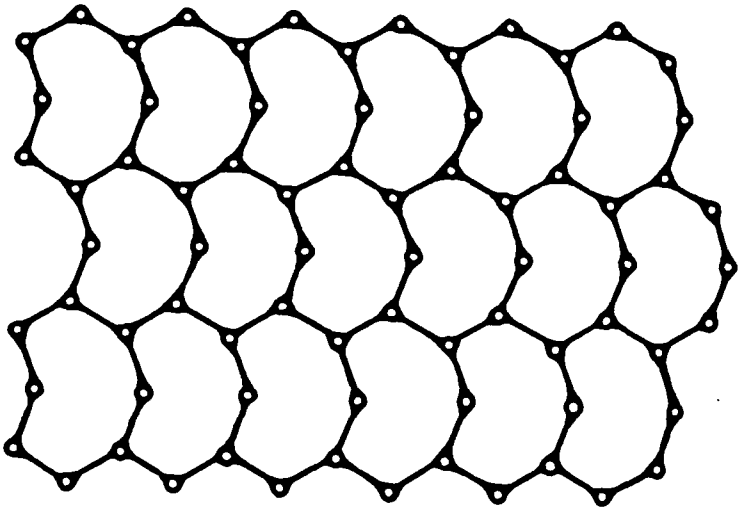

Figure 13: Network of 8-rings

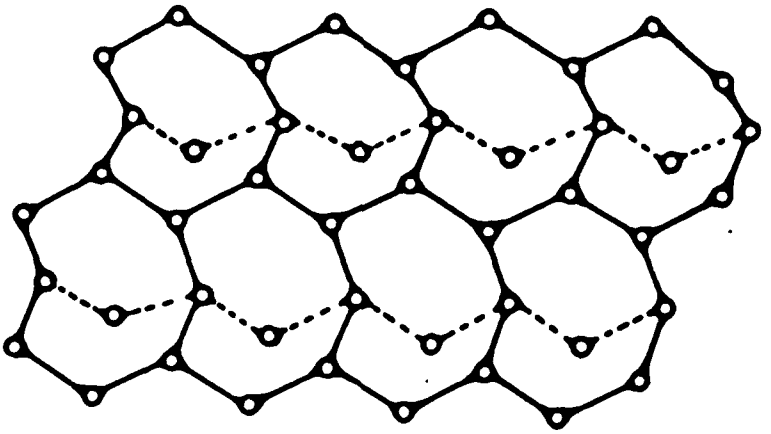

Figure 14: Network of 8-rings in $\beta - BeO$, decomposition of 8-rings into 6-rings is shown by dashed lines

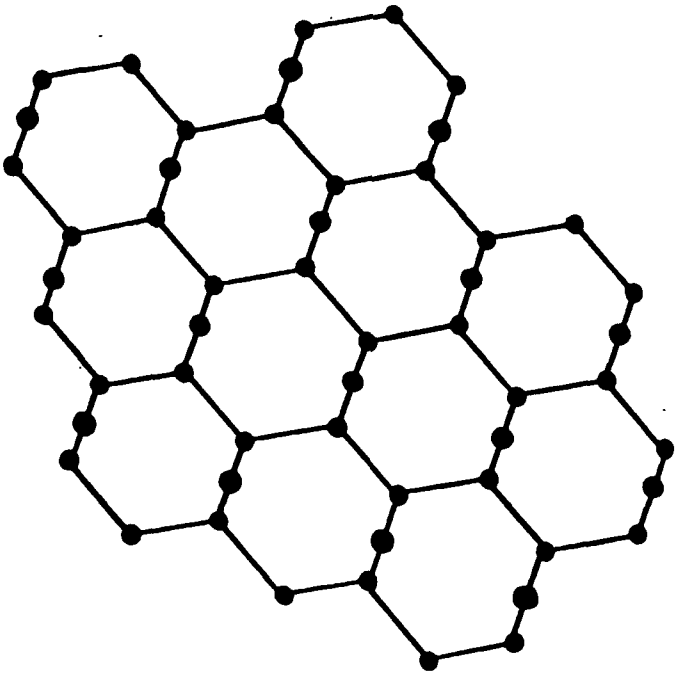

Figure 15: Transformation of the honeycomb network into the 3-connected network of 8-rings.

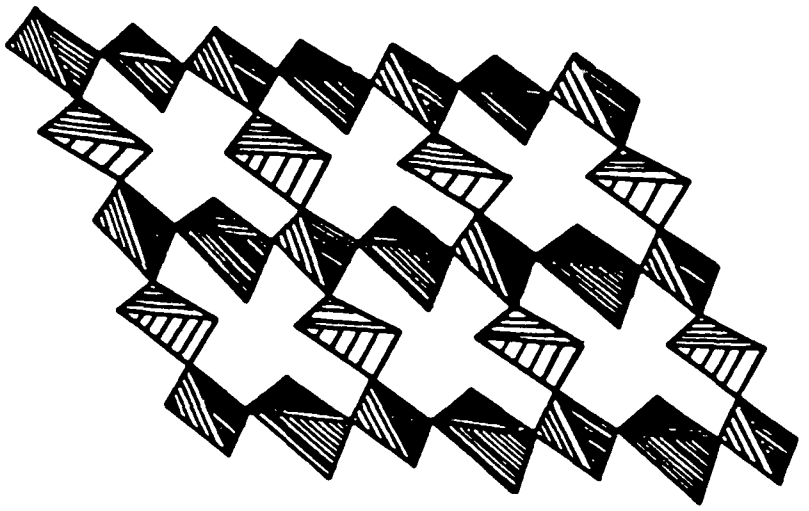

Figure 16: Network of 8-rings in quartz perpendicular to the $[0,0,1]$ direction with nodes represented by tetrahedra

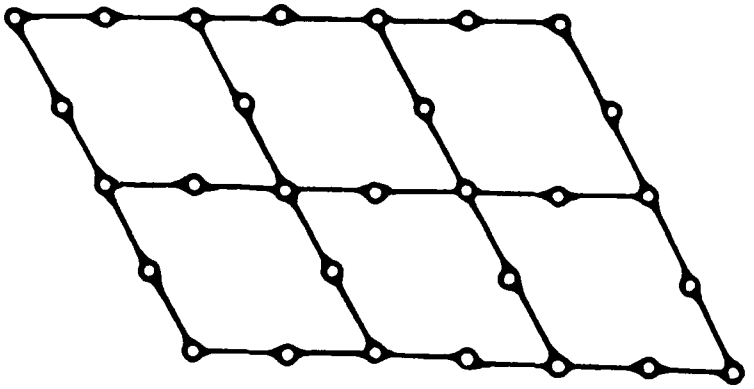

Figure 17: Network of 8-rings in quartz perpendicular to the $[0,0,1]$ direction with nodes represented by balls

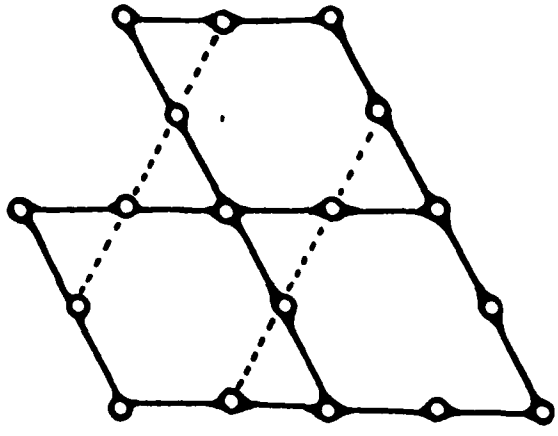

Figure 18: Network of 8-rings in quartz perpendicular to the $[0,0,1]$ direction showing successive planes dashed

Three-dimensional Silica Networks

We return now to glassy silica and networks of tetrahedra whose irreducible rings are 6-rings. The pattern of regular domains interspersed with interfacial glue holds as well in three dimensions as in two, the difference being in the nature of the domains and the glue. The regular domains contain only irreducible 6-rings, the boundary region containing a range of ring-sizes.

The regular domains have the structure of an infinite defect-free 6-ring network. Each layer is a 6-ring triangular network, the triangles are faces of tetrahedra and the tetrahedra alternately stand up and hang down from the network. A pair of such two-dimensional triangular networks are connected together either as in tridymite or cristobalite. The resulting three-dimensional network is a staking sequence of cristobalite-like and tridymite-like layers, the silica version of the large unit cell polytypes found in silicon carbide and many stacking sequences are known. $[SiC_4]$-tetrahedra form the planar units in silicon carbide. The silica network has a two-dimensional unit composed of 6-rings of six Si-atoms linked by oxygen, in silicon carbide the unit is an an alternating chain of 6 atoms, three each of Si and C. Stacking sequences need never repeat in our domains and in that sense need not produce a crystal of the conventional type [15].

A study of the irreducible two-dimensional subnetworks and how they must fit together if formation of defect irreducible rings is prevented underlies our understanding of networks of tetrahedra without irreducible non-6-rings (Recall we refer to irreducible non-6-rings as defect rings.). We note that networks without defect-rings have defect-free irreducible subnetworks. Thus irreducible rings in irreducible subnetworks are 6-rings. We reserve the detailed proofs for the appendix, where we have in addition collected together a complete list of all the definitions which occur in this work.

For the remainder of this section we consider tetrahedral networks in which the irreducible rings are 6-rings. We first observe that an irreducible two-dimensional subnetwork is, as a network, the 6-ring triangular network [Figure 10]. More, a triangle, i.e. a face of a tetrahedron belongs to a 6-ring triangular network. A triangle in this network is a face of a tetrahedron in the three-dimensional network. If the tetrahedra are represented as nodes, this two-dimensional network is the honeycomb network shown in Figure 9. We now show this. As the irreducible rings in an irreducible subnetwork are 6-rings the 6-ring triangular network is the only irreducible two-dimensional network. We need to know that every triangle, i.e. face of a tetrahedron, belongs to a 6-ring network. Later we shall see that a triangle belongs to two 6-ring networks. Now find a 6-ring triangular network containing a fixed triangle. An edge of the triangle belongs to a minimal ring, a ring which cannot be decomposed and so is a 6-ring. A 6-ring belonging to each edge of the triangle is shown

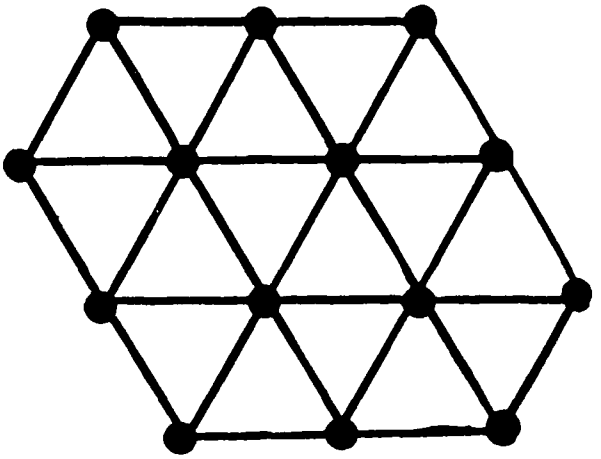

Figure 19: close-packed-plane viewed as a two-dimensional network

in Figure 20.

Each vertex of the triangle in Figure 20 belongs to four edges. Two edges belong to the triangle and each of the two 6-rings to which the vertex belongs contains one of the remaining two edges. A first neighbor tetrahedron of the vertex contains the edges common to the two 6-rings and the vertex. Thus the pair of edges belong to a triangular face of the tetrahedron. The remaining edge of the triangle is shown dotted. Continuing, one finds a 6-ring through each of the *dotted* edges, completing one more layer of 6-rings [Figure 21]. Starting with any triangle in the network, continuation of this procedure results in an irreducible two-dimensional subnetwork through it.

Although the subnetworks we consider are topologically two-dimensional they are not necessarily planar surfaces. This is evident if we consider the tetrahedra whose triangular faces form the irreducible two-dimensional subnetworks. Tetrahedra do not fit in planes. Next we consider the relative orientation of these tetrahedra. We note that surface-bending is required to allow both orientationally varying patterns of tetrahedra and dihedral angles consistent with steric constraints. Two patterns of standing and hanging tetrahedra are seen in Figures 11,12. Some hypothetical motifs are shown in Figures 22,23. Although we do not see a repeat in Figure 23, it may represent a pattern with periodicity larger than the drawing, or part of an infinite non-periodic network. A finite drawing of a non-periodic pattern is not possible of course.

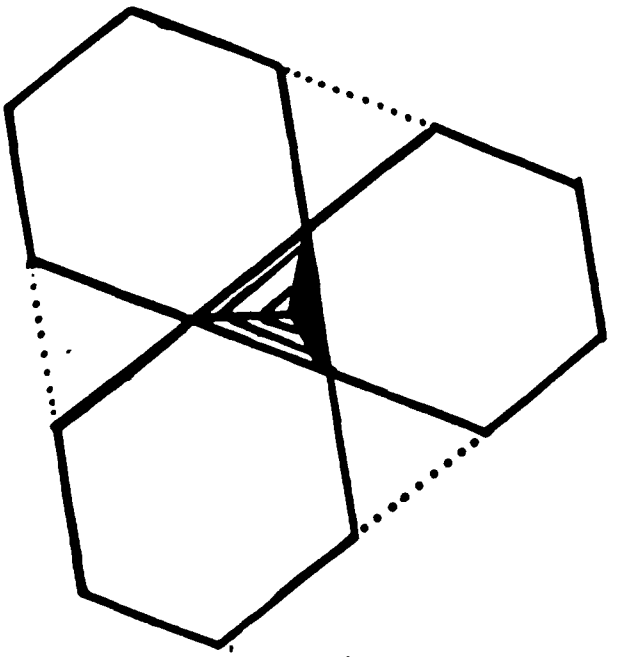

Figure 20: Triangle with one 6-rings through each edge and dotted edge completing faces of first neighbor tetrahedra

We know that in a network with only 6-ring irreducible rings, every edge of every tetrahedron has at least one 6-ring. Intuitively it is seen that if some tetrahedra had an edge with only one 6-ring the network would be quite strained near this tetrahedron. Many models were constructed in a vain attempt to build a network with only 6-rings and no periodicity in any direction.

In a network where irreducible rings are 6-rings, each tetrahedron has exactly twelve 6-rings, two through each of its edges. This is shown in the appendix. From the proof of this result we know enough of the relative arrangements of these twelve 6-rings to show that in the sterically interesting cases there are (up to network equivalence) four possible local clusters. We explicate below, but first we illustrate the one arrangement of tetrahedra which we exclude, this being a pair of 6-rings which pass through each other as shown in Figure 24.

It is a theorem from the geometry of networks of tetrahedra whose irreducible rings are 6-rings that each tetrahedron has a face with a two-dimensional 6-ring subnetwork of alternating tetrahedra as shown in Figure 11. All that we require of this network is that the first-neighbors of the center of the local cluster have reverse orientation. We note that all of the faces of a tetrahedron in cristobalite satisfy this condition, but only one face of a tetrahedron in tridymite has this property. Using this result we can view the local cluster of a tetrahedron as comprised of a two-dimensional section, shown from both the top and

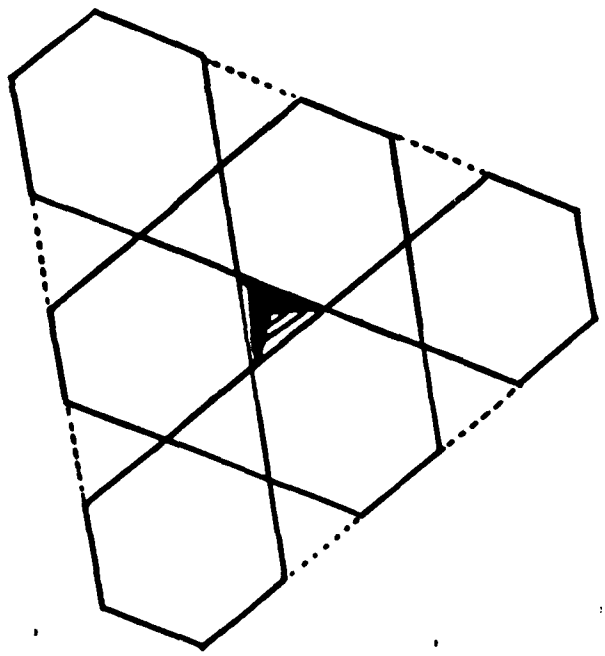

Figure 21: 6-rings through first neighbors

bottom in Figure 25, together with the connecting-rings above and below this section. Further it is seen that once one tetrahedron has been connected above the section then the connectivity of the network, lack of intertwined rings and two 6-rings per tetrahedral edge completely determine the connections of those of the other tetrahedra in the local cluster above this section. The same argument for the tetrahedra below the base plane shows that once one tetrahedra is connected the connections of the others are completely determined.

There are four possible local clusters composed entirely of 6-rings and embedable in a 6-ring infinite network. To see this we observe that there are two ways of completing the local cluster above the base plane and two below as shown in Figures 26,27. These correspond to the stacking sequences of cristobalite and tridymite, whence our somewhat sloppy reference to cristobalite-like and tridymite-like layers in the one-dimensional crystal described earlier.

We have the local structure of an irreducible 6-ring network. It remains to note that if once either a cristobalite-like layer or tridymite-like layer has formed then the entire rest of that layer must form similarly in order that the network be a one-dimensional crystal. For this purpose it is enough to observe that the formation of a tridymite like configuration on any layer forces the entire rest of that layer to form in the tridymite network configuration. A proof of this is given in the appendix.

We conclude that a network whose irreducible rings are 6-rings is a one-dimensional network-crystal with a preferred orientation. The two dimensional irreducible subnet-

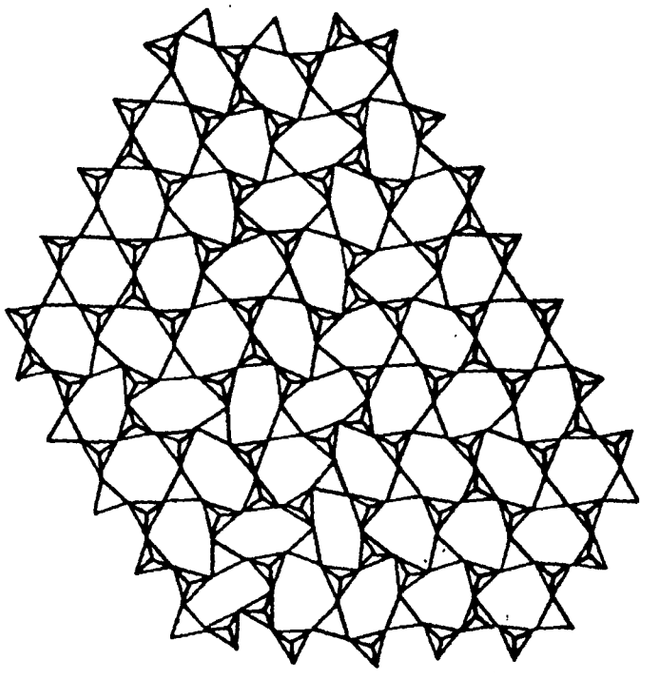

Figure 22: A periodic pattern of upward and downward pointing tetrahedra on the 6-ring two-dimensional triangular crystal which is distinct from those which occur in tridymite.

works *orthogonal* to that direction are the 6-ring two-dimensional triangular crystal whose tetrahedra have alternating orientation. Each successive layer is either like cristobalite or tridymite. The proof of this result has been detailed. It converts speculations concerning the structural possibilities into a theory which lies on much firmer ground.

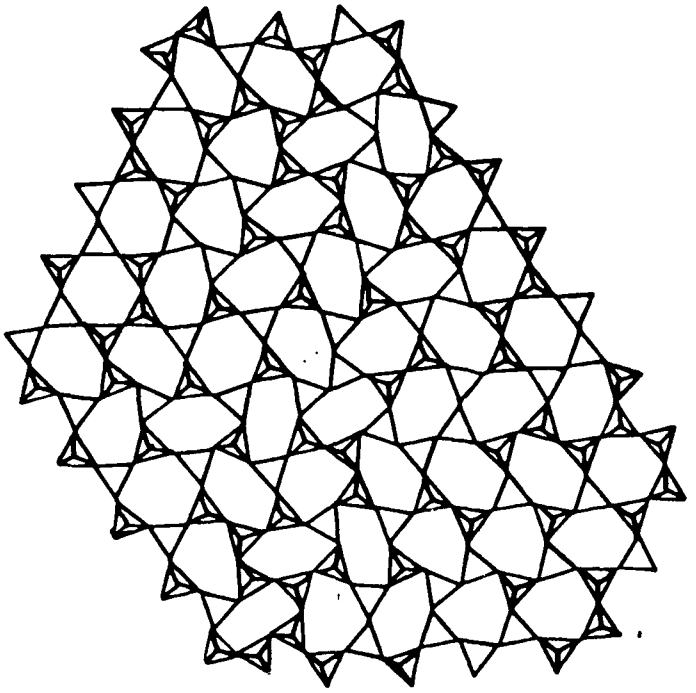

Figure 23: A pattern of up and downward pointing tetrahedra which has no apparent periodicity.

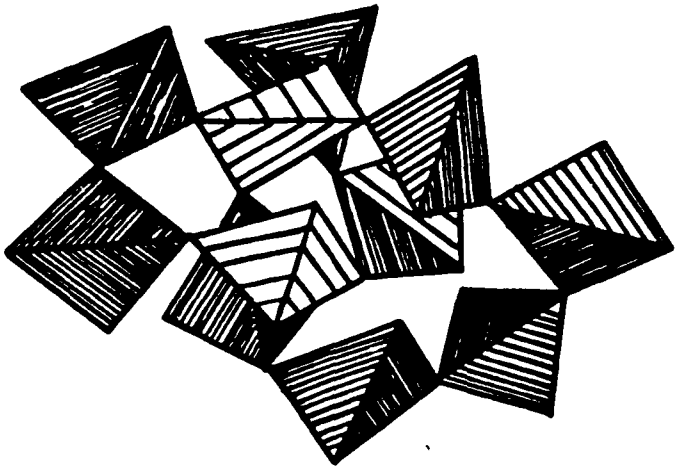

Figure 24: A pair of 6-rings which are pass through each other.

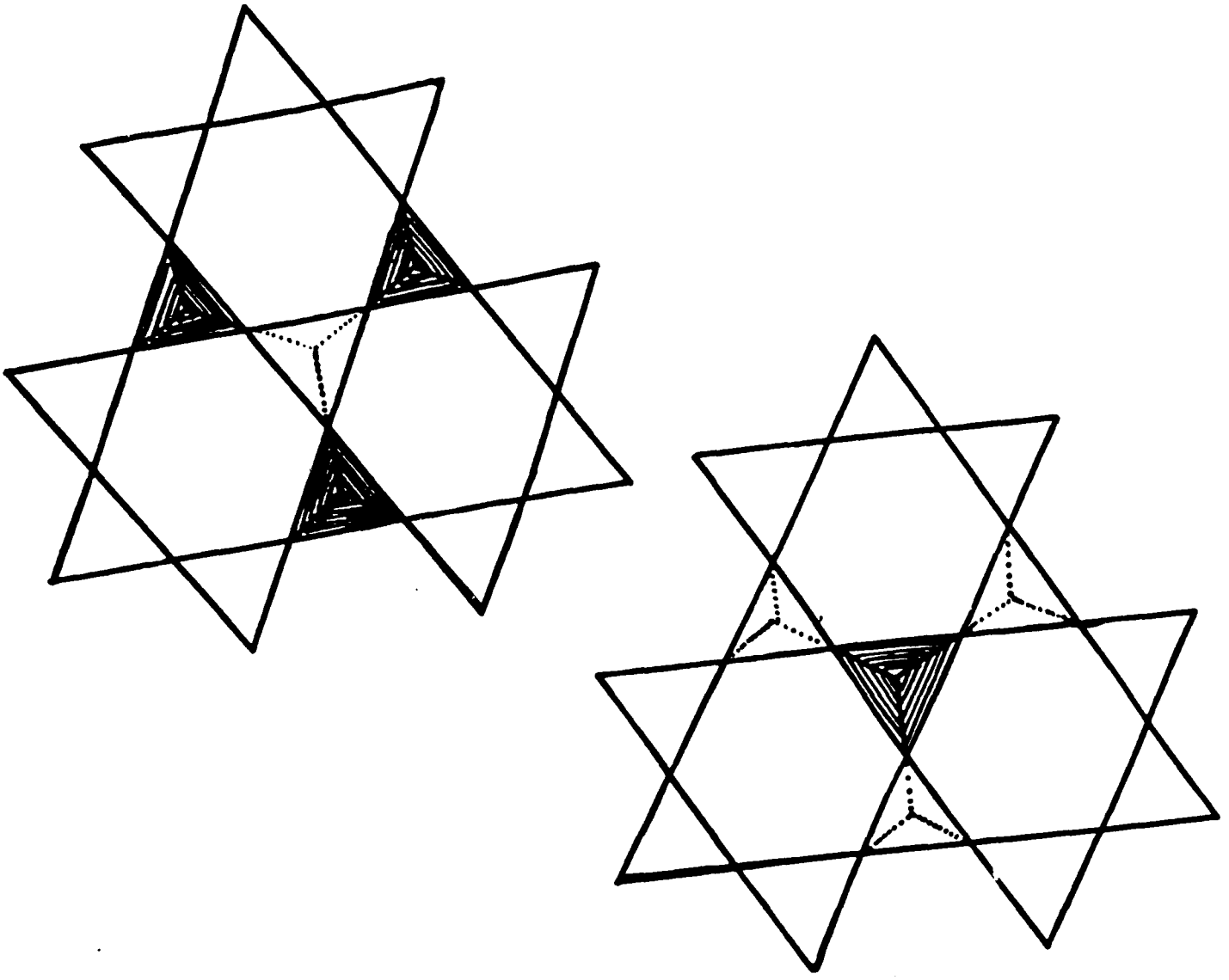

Figure 25: Top and bottom view of the distinguished two-dimensional section in the local cluster of a network with only irreducible 6-rings.

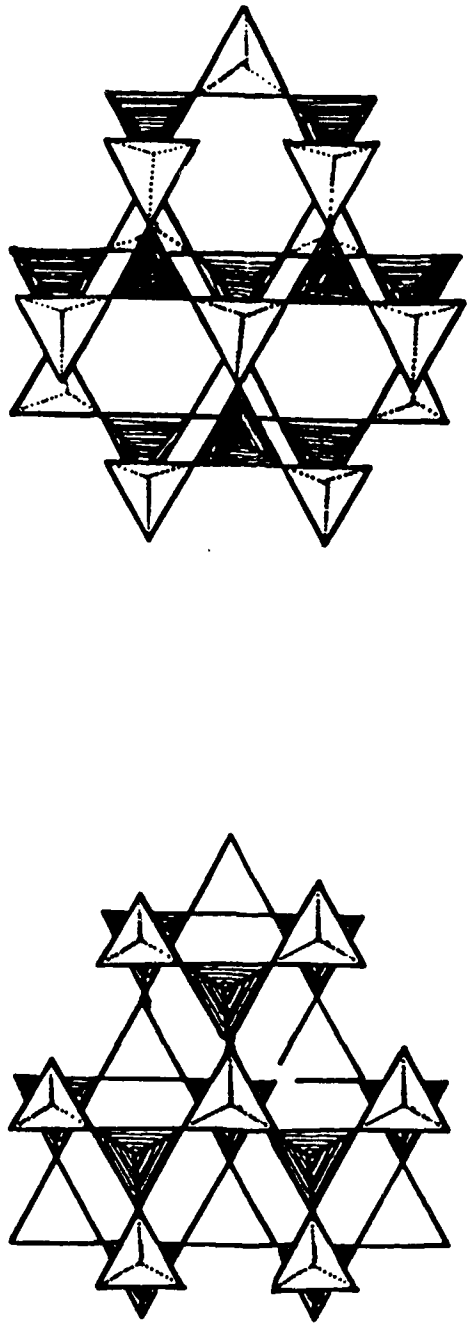

Figure 26: The two completions of the local cluster above the basal two-dimensional subnetwork.

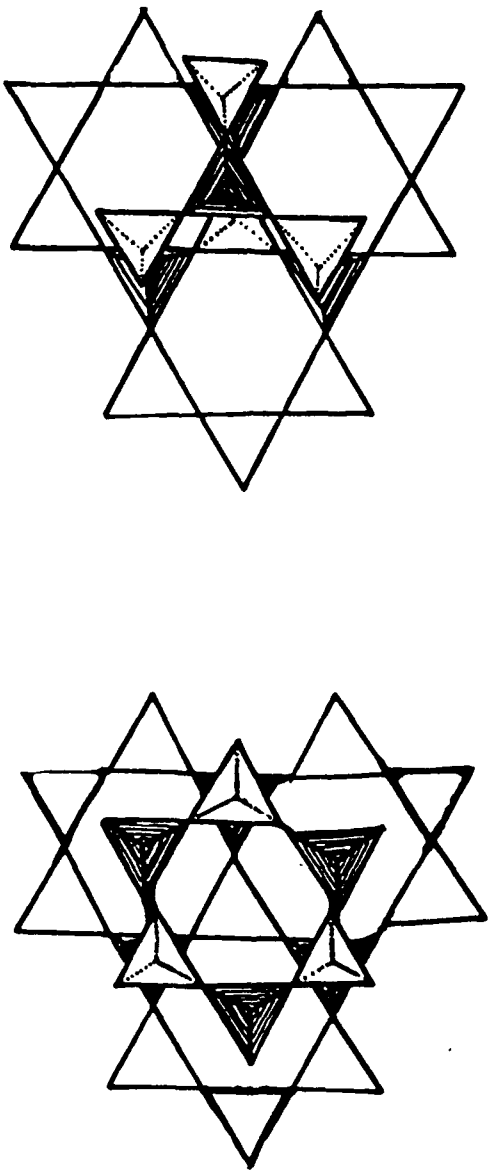

Figure 27: The two completions of the local cluster below the basal two-dimensional subnetwork.

General Network Glasses

The *modulated network model* for silica glass structure presented here can be considered heir to both the continuous random network model due to Zachariesen and the micro-crystalline model with some aspects of the paracrystalline model too. It is now possible, with the language we provide to partially classify the local structure of a network, and in special cases the global structure. The continuous random network model posits a continuous variation of dihedral angles, but is eloquently silent about the detailed network structure. Our model differs from the continuous random network model in proposing a specific picture of the local network structure. More, there is no discrete boundary between the more and less ordered regions. Additionally the ordered regions are not crystalline.

For the melt cooled silica glasses, we assume that the network structure is dominated by 6-rings. The ordered regions as a stacking sequence of cristobalite-like and tridymite-like layers are regular as a network. They have the same connectivity as the crystalline layers. Observe that while each layer of the network is periodic and in that sense crystalline, the material is not a crystal, since the cartesian atomic coordinates are not periodic. The regular regions in our model even if infinite would not be crystals, the two-dimensional subnetworks are periodic as networks only, as imbedded in space they are curved. Thus, while our model has the regular regions of the micro crystalline model, these regions are not crystalline. The lack of sharp well defined interfaces in our model follows the continuous variation of properties of the continuous random network model.

We now discuss the relation between the structure and distribution of the regular regions for silica glasses, the relative proportion of the regular and interfacial regions and the distribution of the non-6-rings. We consider extensions of this model to non-silica network glasses and to silica glasses with various size rings. A silica network with irreducible rings (6-rings) would be a one-dimensional crystal rather than a glass, and it would have the appropriate discrete diffraction pattern of a disordered crystal. We can, as with the two dimensional example, imagine euclidean-three-space with the non-6-rings marked. Then any convex region which contains no mark contains a network which is *almost* a one-dimensional crystal. Almost refers to the fact that as it isn't infinite it can't be periodic and can't be a crystal. Our proof was based on knowing the local cluster of a tetrahedron embedded in a network that to third network neighbors contained only 6-rings. Thus our proof applies equally to any part of a network such that all its tetrahedra have their third network neighbors within three tetrahedra of the boundary of a convex region containing no defect-rings. The boundary can be three tetrahedra thick and can be quite disordered, the ordering of the planes need not observe the preferred direction of the axis of the one dimensional crystal, though it must contain only 6-rings.

We built small networks, which except for the surface, contained no defect-rings and had an allowed local cluster at each tetrahedron within two tetrahedra of the center. We thought of these models as glasses as they showed no incipient periodicity. The orientational preference was not yet visible as such a network if convex, has a diameter of eleven tetrahedra, at 0.2nm [tetrahedral edge] that gives a diameter of the ball of 2.2 nm. If the tridymite-like layers are near the surface, then there are only 10 layers, excluding the surface tridymite layer. Cristobalite itself has a higher symmetry than tridymite, and as a result cristobalite layers do not as easily reveal the prefered direction of the layered structure. With the surface three tetrahedra thick this gives a ball seventeen tetrahedra in diameter, or 3.4nm. Our conjectures on the scale of the regular regions is partially based on these models together with the above computation.

The regular regions have a preferred direction, that of the tridymite and cristobalite like layers. Each region has a regular network with network-periodic layers but the atomic positions in the layers are not correct as planes undulate and angles are distorted. Associated with such crystalline distortions are increases in energy which are balanced by the ease of fitting several regions together with minimal interfacial material. Larger regular regions are more strained having higher cost per bond for atomic plane-bending. This comes about since a curved plane has elongated bonds. However, the plane above has higher curvature, thus a larger increase in bond lengths as shown in Figure 28 for the same degree of distortion. This model depends on the relatively soft $Si-O-Si$ angles to permit the distortion necessary to get complete matching at the interface. The planes in the regular region are curved, however the sense of the curvature changes, its sign is not constant for any plane throughout a particular region. Both tridymite and cristobalite are often shown in models in an idealized configuration with angles of 180^0, however cooperative twists of the angles allows both of these structures the more accepted dihedral angles of 144^0. Similar cooperative distortions permits domains of our model to form with a wide range of $Si-O-Si$ angles. This is a broadly drawn model with much freedom, which can accomodate many choices of bond angle distribution. The size of the regular domains and the relative proportion of material in the regular domains and interfacial material will certainly be affected by the bond-angle distribution assumed. Soft $Ge-O-Ge$ angles are also found and thus our model, although directed here towards the structure of silica glass, is equally applicable to that of germania [7].

Changing the viewpoint, orientation within the region also limits the size of the regular regions. Larger regions generally have smaller curvature. The area of near contact between adjacent large regions will be greater. A larger contact area increases the influence of nearby regions thus increasing the probability of forced orientational conformity between

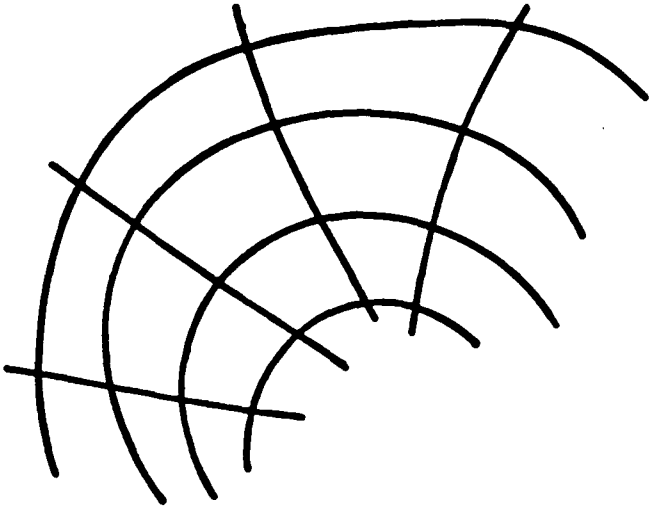

Figure 28: Bending of atomic planes showing increase in excess bond length in successive atomic planes

nearby regions. An assemblage of nearly regular regions knitted together with irregular interfacial material will not have, in diffraction, the sharp peaks of a crystalline material *if there is no correspondence between the preferred directions* in the regular regions. A useful image is that of large rocks held together by mortar comprised of smaller rocks, held together by smaller rocks and on and on.

We now have to ask whether there are any irreducible rings other than 6-rings, how and when they form and what determines the relative fraction of 6-rings and non-6-rings. We expect the melt-cooled silica glass to be dominated by irreducible 6-rings by analogy with the high temperature silica polymorphs tridymite and cristobalite whose only irreducible rings are 6-rings. We visualize the regular domains forming independently with interfacial material condensing as regular regions impinge on each other.

For a given distribution of ring sizes, what size are the near-regular domains and how much interfacial glue is there? To answer, one needs further information. Knowledge of the distribution of the defect-rings and degree of regularity of the domains would suffice. The degree of regularity of the domains is significant as a small number of imbedded defect-rings in a region could relieve a considerable amount of stress due to enlarged and bent bonds while preserving a good distribution of angles and a near conformality to the four allowed local clusters of 6-rings. If that were the case the resulting structure might be found to have isolated defect-rings and an interfacial region with many non-defect-rings.

At the opposite extreme to the picture of isolated defect-rings is one where condensed defect-rings form a continuously connected subnetwork analogous to a second phase. This would be expected if, for example the volume fraction of defect-rings were of a similar order of magnitude as the fraction of non-defect-rings. Using the very coarse analogy used earlier this process might be considered as the generation of a quartz as one phase and cristobalite/tridymite as another.

Finally it is worthwhile to investigate the breath of applicability of our model. It is based on two requirements. The first is a fully bonded network and the second is the flexibility of the $Si - O - Si$ angle around some equilibrium position. The second consideration applies to silicate materials in general and also as we have already noted to GeO_2 as well. The first requirement though is much more restrictive. The effect on glass formation of other elements (such as boron) has long been studied. Because of the differences in electronic structure (three rather than the four valence electrons found for silicon) networks containing boron may not be fully bonded in the sense of our discussion here. Extension of the ideas used here to other glasses is to be expected. The actual structure of the various regions and the degree of differentiation between the various regions will depend on the particular geometry that is set by the chemical bonding demands of the network. Of particular interest may be the fractionation of elements into various parts of the glass depending upon these criteria. For example elements which lead to much stiffer $T - O - T$ angles will preferentially be located in those areas where the angle strain is least.

Acknowledgement

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Appendix

Definitions:

Definition 1 *[Tetrahedral Network] A Tetrahedral-network (network of vertex-sharing tetrahedra) is comprised of tetrahedra connected only at vertices. No face or edge sharing nor any other intersections between tetrahedra are allowed. In addition each vertex belongs to exactly two tetrahedra and the tetrahedra of this network are equal regular tetrahedra. As a graph this is equivalent to a four-valent graph, a graph in which each node belongs to four edges. The tetrahedra are viewed as nodes and the vertices of the tetrahedra as edges.*

Definition 2 *[path] A path, in a graph is a collection of edges which are connected to each other. In a tetrahedral-network a path is comprised of either a collection of tetrahedra or a collection of edges.*

Definition 3 *[path length] The length of a path is the number of its edges.*

Definition 4 *[path distance] The path distance between two nodes in a graph is the path length of the shortest path connecting them. Equally it is the minimum of the path lengths of all possible paths connecting the two nodes. If there is no path connecting the two nodes the path distance is taken to be infinite.*

Definition 5 *[ring] A ring is a closed path. Alternatively a ring is a path whose two end points are the same.*

Definition 6 *[Reducible Ring] Two paths in a ring are defined by any two of its nodes which are distinct. The shorter of these paths gives a path distance for these two nodes* in the subnetwork comprised of the ring. *If for any two nodes in the ring the path distance restricted to the ring is larger than the path distance between the nodes in the network the ring is reducible.*

Definition 7 *[Irreducible Ring] A ring is irreducible if it is not reducible. Thus a ring is irreducible if there is no shorter path in the network connecting the two nodes than is found in the ring.*

Definition 8 *[Ring Cluster] The* ring cluster *of a node in a network is the subnetwork comprised of the nodes and edges of all irreducible rings containing that node. The ring cluster of a node is the smallest subnetwork containing all the primitive/irreducible rings of the node.*

Definition 9 *[N-ring] An N-ring in a graph is a ring with N edges.*

Definition 10 *[sum of rings] The sum of two rings R_1 and R_2 is a ring which has as edges any edge belonging to either R_1 or R_2 but* not *to both. The vertices of the edges of the sum are its vertices.*

Definition 11 *[reducible ring (alternate definition)] An N-ring is reducible or decomposable if it is the sum of two smaller rings.*

Definition 12 *[two-dimensional subnetwork] A two-dimensional subnetwork is a subnetwork which has an embedding into a two-dimensional surface.*

Definition 13 *[Minimal/Irreducible Two-Dimensional Subnetwork] A two dimensional subnetwork is minimal or irreducible if all of the rings in the subnetwork are irreducible as rings considered in the original network.*

Definition 14 *[graph map] A graph map is a function from the vertices and edges of one graph to those of another graph. It must preserve incidence, meaning that an edge connecting two vertices has as its image an edge connecting the images of the respective vertices.*

Definition 15 *[Network equivalence] A graph map which is one-to-one and onto, i.e. which has an inverse is said to give a network equivalence between the two graphs.*

Irreducible Two Dimensional Subnetworks

The desire to understand the structure of complex three-dimensional objects via simpler low dimensional entities is seen in the popularity of close-packed-planes as a descriptive tool. So strong is this wish that often non-planar sections of crystal are described in terms of imaginary close-packed-planes with systematic absences.

We present an alternative formalism which generalizes the ideas underlying the concept of close-packed planes to open network structures. In a close-packed structure the close-packed planes are those with the highest packing density. These planes are also understood as being maximally bonded, where by this we mean that the ions in these planes have the largest fraction of their bonds within the plane rather than connecting to ions in other planes. As a replacement for this we take two-dimensional subnetworks which are maximally connected. We will understand this to mean that if a pair of ions in the network is connected by a path of length n then it is also connected by a path of that length in the subnetwork. Ions do not become further apart in the subnetwork then they were in the network, and this is the sense in which the subnetwork has sufficient bonds. In close-packed structures the close packed planes are the irreducible two-dimensional subnetworks. In cristobalite and tridymite, the networks of 6-rings are the irreducible two-dimensional subnetworks.

We begin with the definition of an irreducible ring, a central concept. A ring is reducible if it decomposes into two smaller rings such as the 8-ring which decomposes into two 6-rings in Figure 29. A ring is irreducible if it cannot be so decomposed as in [Figure 30].

To define an *irreducible two-dimensional subnetwork* we must explain both what we mean by two-dimensional for a subnetwork of a graph and when such a network is irreducible. A subnetwork is two-dimensional if it it embedable in a two-dimensional surface such as R^2. Intuitively, a subnetwork is irreducible if it is composed of irreducible rings. This can be formalized either by saying that each node of the subnetwork belongs to an irreducible ring contained in the subnetwork. Alternatively a subnetwork is irreducible in the same way as a ring: The length of the shortest path connecting two nodes of the subnetwork is not larger than a shortest path in the network — path distance in the subnetwork is the same as in the network.

The irreducible rings in a close-packed structure are 3-rings and the irreducible two-dimensional subnetworks are those which contain only 3-rings. In general the planes, or *distorted planes*, of densest packing in a structure which can be described as having close-packed-planes with systematic absences will be the irreducible two-dimensional subnetworks.

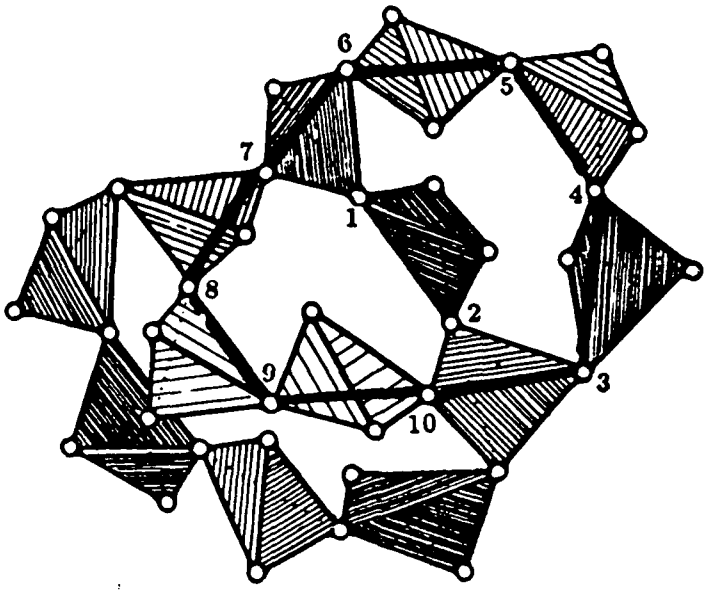

Figure 29: Example of an 8-ring which decomposes into two 6-rings.

It is recognized that a near close-packed array of atoms is an appropriate focus for the structure of a crystal in which it occurs. A further step is to focus entirely on irreducible two-dimensional subnetworks, independent of their conformational correspondence, or lack, to a plane. Irreducible two dimensional subnetworks are not topologically planar. Cylindrical subnetworks occur in quartz and more notably in the zeolites. To understand the structure of a crystal, or network, from its irreducible two-dimensional subnetworks one must know the generating scheme that fits together the two-dimensional subnetworks to form the three-dimensional network structure.

It is important to observe that just as a ring is irreducible only in the context of the network which contains it so a two-dimensional subnetwork is irreducible as a subnetwork of a particular three-dimensional network. Irreducibility is a statement about a relationship between a ring and a network or a subnetwork and a network.

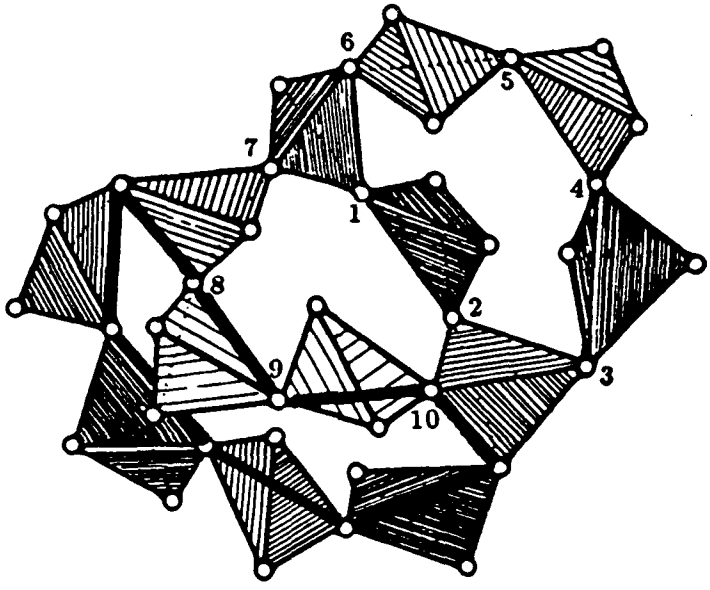

Figure 30: Example of an 8-ring which is indecomposable.

The local cluster in a network where primitive rings are 6-rings.

We begin the classification of 6-ring-tetrahedral networks with an investigation of their local structure (A tetrahedral network is a network of vertex-sharing tetrahedra with the usual constraints. (Two tetrahedra per vertex, no other intersections between tetrahedra.) A six-ring network is one in which the irreducible rings are 6-rings.)

In a tetrahedral 6-ring network each tetrahedron has twelve 6-rings two of which belong to each of its edges. We sketch the proof of this result. The two parts of this proof are:

1. A tetrahedron in a 6-ring-tetrahedral network has a face belonging to a 6-ring-triangular network [shown in Figure 10] with orientationally alternating tetrahedra [Shown in Figure 11].

2. Utilizing this alternating 6-ring-triangular network-crystal the 6-rings and their configurations are located.

The existence of a face belonging to an alternating triangular 6-ring crystal.

We assume that T_1 is a tetrahedron and no face of T_1 belongs to an alternating triangular 6-ring crystal. Each face of T_1 has a first neighbor tetrahedron T_2 such that T_1 and T_2 have the same orientation on any 6-ring crystal. It follows that the vertical edges of T_1 (the edges of $T1$ containing the common vertex of T_1 and T_2) each has one 6-ring as shown in Figure 31.

A pair of 6-rings through T_1 and T_2 together with a third neighbor T_3 of T_1 are shown in Figure 32. It is seen from this figure that a second 6-ring through a vertical edge of T_1 would result in a two-dimensional-6-ring crystal with T_1 and T_2 on opposite sides contrary to the hypothesis.

As the hypothesis is that no face of T_1 lies on a two-dimensional crystal with alternating tetrahedra, we conclude that there is a second first-neighbor T_4 which must also be on the same side as T_1 on every two-dimensional crystal containing their common vertex. T_1 together with these two first-neighbors are shown in Figure 33.

It is seen from figure 33 that five of the six edges of T_1 must have one 6-ring and the configuration of 6-rings through T_1 must be as shown in Figure 34.

Construction of this configuration with regular equal tetrahedra is not possible.

Twelve 6-rings

A tetrahedron has a two-dimensional-6-ring-crystal on which the tetrahedra alternate. This network is shown in Figure 11. The first neighbors of some upward pointing tetrahedra, a

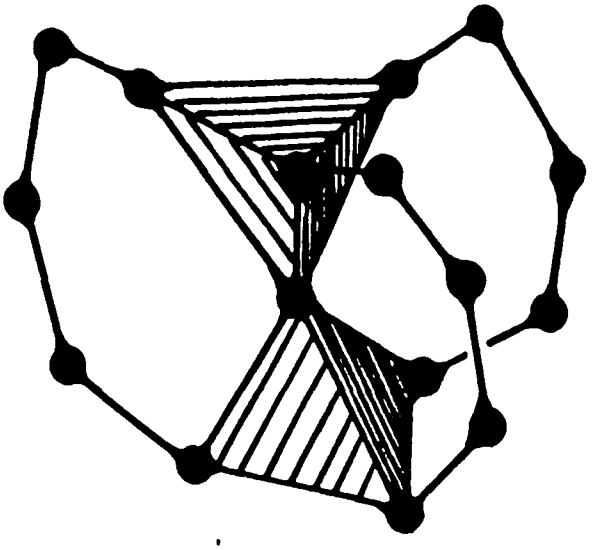

Figure 31: The three 6-rings through the vertical edges of T_1

tetrahedron and its second-neighbors, are shown in Figure 35.

Utilization of the fact that the irreducible rings are 6-rings, it is shown that the first-neighbors of the upward pointing tetrahedra must also belong to a two-dimensional 6-ring triangular network-crystal. Similarly, for the first neighbors which fall below the network. From the existence of these two triangular networks, follows the four possible configurations and the existence of twelve 6-rings.

The four possible configurations derive from the two possible choices, tridymite-like or cristobalite-like stacking, on each of the two sides of the 6-ring network with alternating tetrahedra.

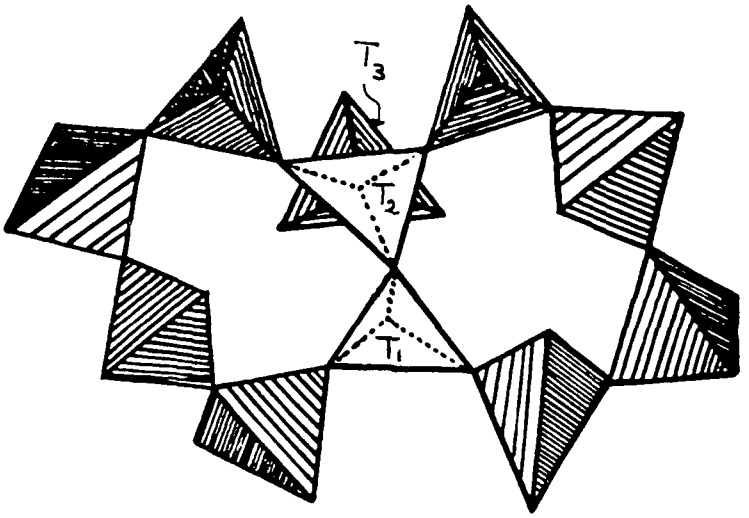

Figure 32: Tetrahedra T_1 and T_2 and a third-neighbor tetrahedron T_3. The two-dimensional 6-crystal surface on which T_1 and T_2 sit with the same orientation is shown, and two of the 6-rings through vertical edges of $T1$

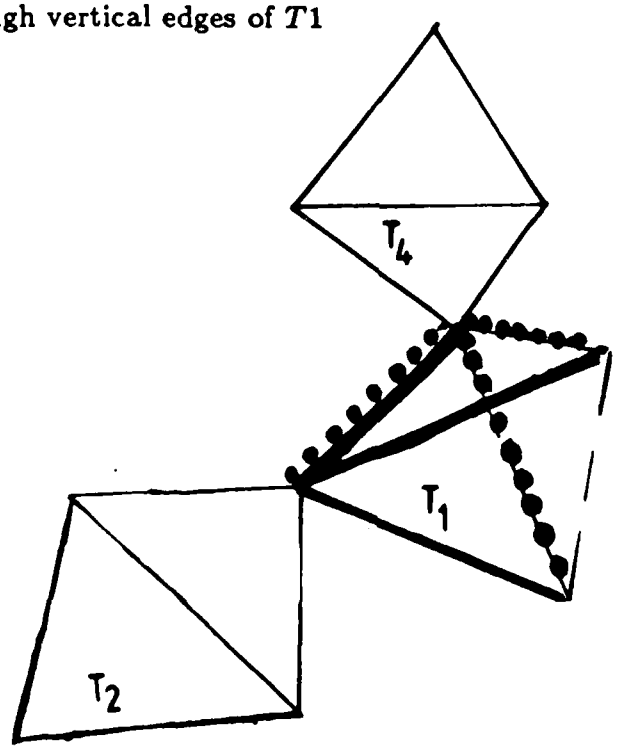

Figure 33: The two first-neighbors of T_1 which must each have the same orientation on any common two-dimensional surface. Each such first neighbor determines three edges of T_1 each of which has one 6-ring, they are shown respectively bold, and dotted.

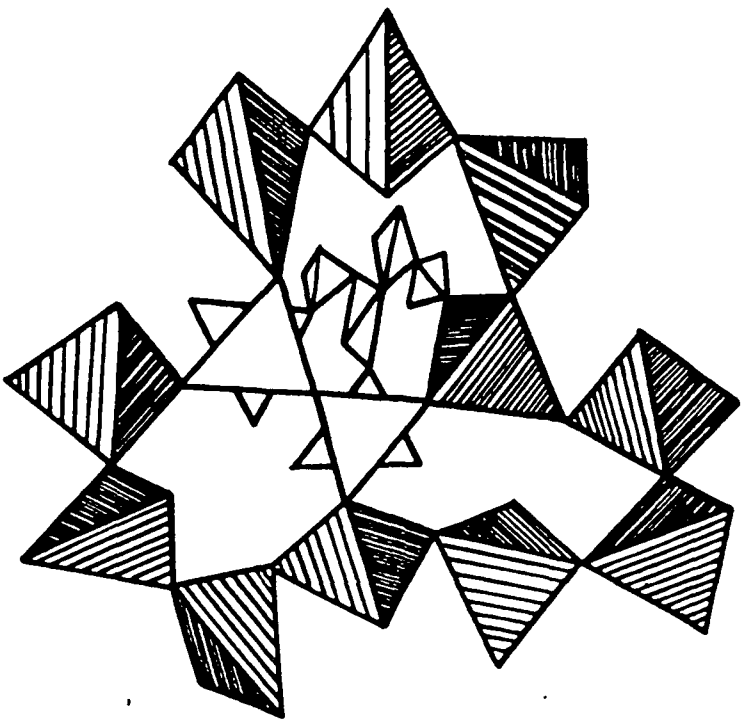

Figure 34: The configuration of 6-rings through five of the edges of T_1 that is forced by the condition that T_1 has no two-dimensional 6-network-crystal surface with alternating first neighbors through any of its faces.

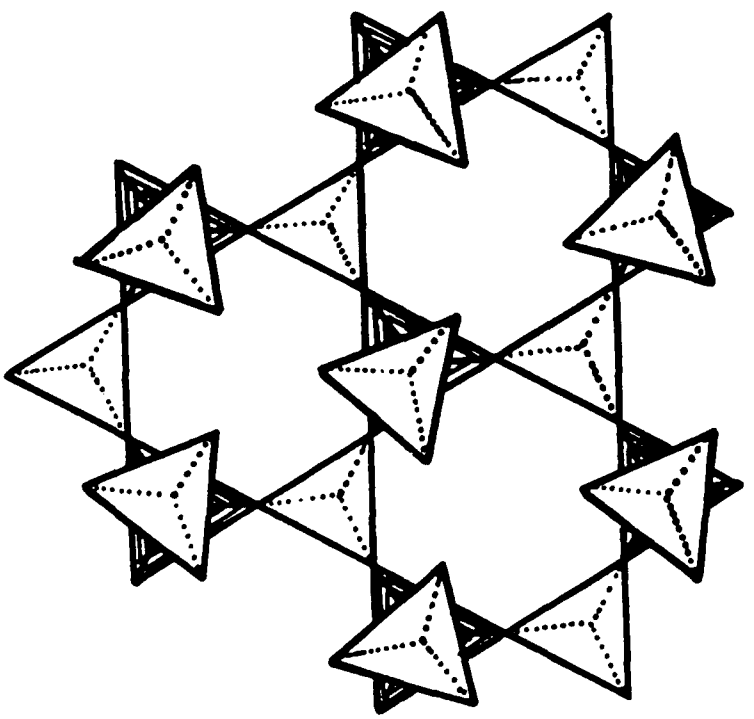

Figure 35: Alternating tetrahedra on the two-dimensional-6-ring-triangular crystalline network, showing the six fourth-network-neighbors of a tetrahedron.

The local cluster of a first neighbor

The four possible local clusters which can occur in a 6-ring tetrahedral network have been enumerated. To see that a network is formed of tridymite and cristobalite like layers it suffices to see that starting with one tetrahedron and its distinguished subnetwork a tridymite like configuration results in a similar configuration at the first-network neighbors in the distinguished subnetwork. A network refers to a 6-ring tetrahedral network. Its distinguished two-dimensional subnetwork is the 6-ring triangular network-crystal on which first neighbor tetrahedra have opposite orientation to each other. We abbreviate distinguished two-dimensional subnetwork to distinguished subnetwork. As there are two possibilities, if tridymite once is tridymite always it will be the same for cristobalite.

The argument is based on the following:

1. The local cluster of a first neighbor contains all rings common to the tetrahedra and its first neighbor. Thus the locations of half the rings of the first neighbor are known from the original local cluster. The local cluster of the first neighbor must satisfy two constraints; it is one of the four possible local clusters and it contains the required fragment of the original local cluster.

2. There is a network configuration which occurs in tridymite and not cristobalite and vice versa.

We label the central tetrahedron of the first cluster T and the first-neighbor tetrahedron in the distinguished two-dimensional subnetwork S. The subnetwork is called N. There are two cases to consider, the two possible orientations of T on N. Configurations which occur only in cristobalite (Figure 36) and tridymite (Figures 37,38) are shown.

Case I T points up

We have the tetrahedron T and first neighbor S as shown in Figure 39, whence we observe a configuration of the form shown in Figure 37.

The configuration in Figure 37 occurs when a third-network neighbor of S has three 6-rings in common with S. There is only one way for this configuration to occur in any of the four allowed local clusters and in this case it is with the face of S lying in N as the face defining the distinguished subnetwork N. Thus S and T have the same distinguished subnetwork, and that part of the network defined by S now has the required form.

For the case where T points up, we now know that the local cluster of any first neighbor in the two-dimensional subnetwork is also tridymite like.

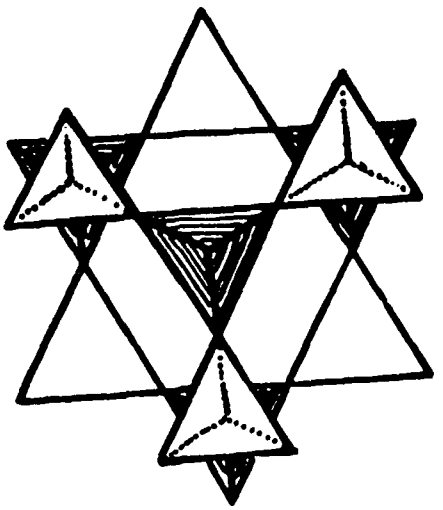

Figure 36: A configuration which occurs only in cristobalite.

Case II T points down

We have the distinguished two-dimensional subnetwork N and tetrahedra T with first-neighbor S as shown in Figure 40.

As before we know see that the local cluster of S contains the tridymite-like configuration of Figure 37, which is nowhere to be found in a cristobalite-like local cluster. Thus the local cluster at S is not cristobalite. More, the first neighbors labeled 1 and 3 of S in Figure 41, which are second neighbors of T must point down as T does in order to give the correct configuration on the reverse side of N for the local cluster of T. They must point down independent of which configuration is on the other side, both make this same demand.

With the configuration as shown in Figure 41, there is only one way to get the required two 6-rings through the vertical edge A of S, this is through the two first-neighbors attached to A labeled 1 and 2 as shown in Figure 42.

The two second neighbors shown in Figure 42 must have the two 6-rings of edge A. This is so as the other first-neighbor of 1 lies below the plane and so cannot have a 6-ring through 2. Thus the two 6-rings must be as shown in Figure 43.

If the edges of the two 6-rings in Figure 44 are now replaced by tetrahedra, the result is that part of the configuration shown in Figure 37 through the edge A and the two first neighbor tetrahedra 1 and 2. The same argument for the edge B shown in Figure 45

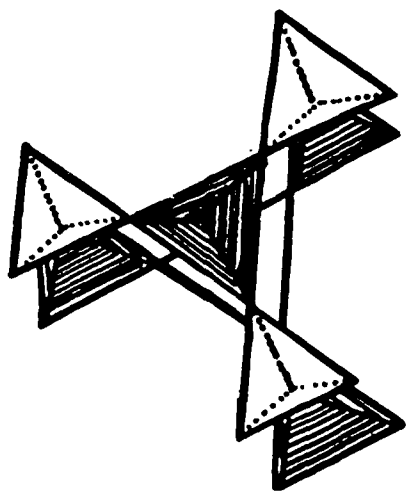

Figure 37: Configuration 1 which occurs only in tridymite.

completes the tridymite-like arrangement of a local cluster for the tetrahedron S. It also completes the argument that tridymite like at T forces tridymite like at S.

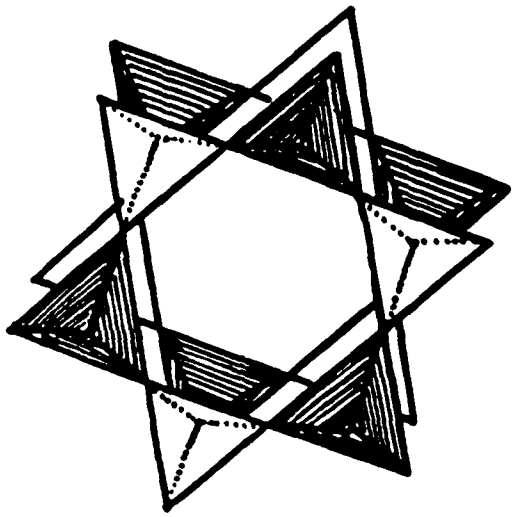

Figure 38: Configuration 2 which occurs only in tridymite.

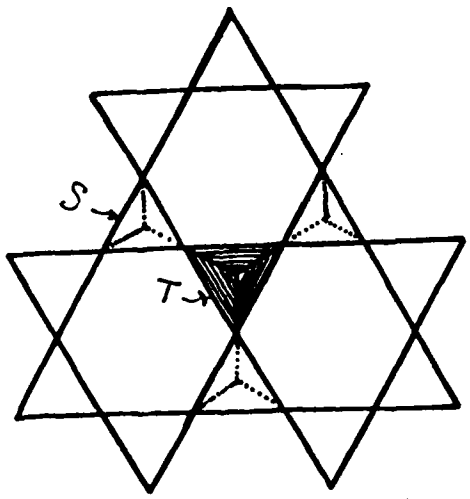

Figure 39: Upward pointing tetrahedron T and first neighbor tetrahedron S on distinguished two-dimensional subnetwork N.

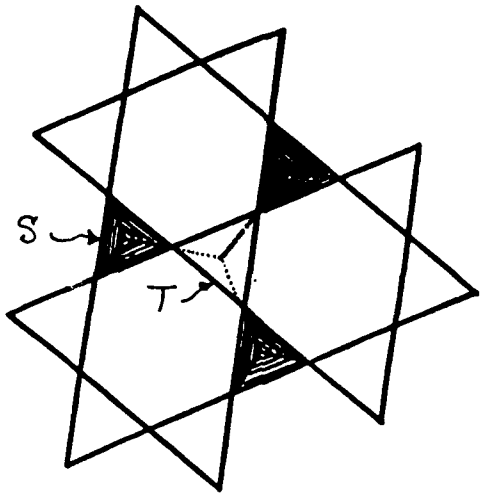

Figure 40: Downward pointing tetrahedron T and first neighbor tetrahedron S on distinguished two-dimensional subnetwork N.

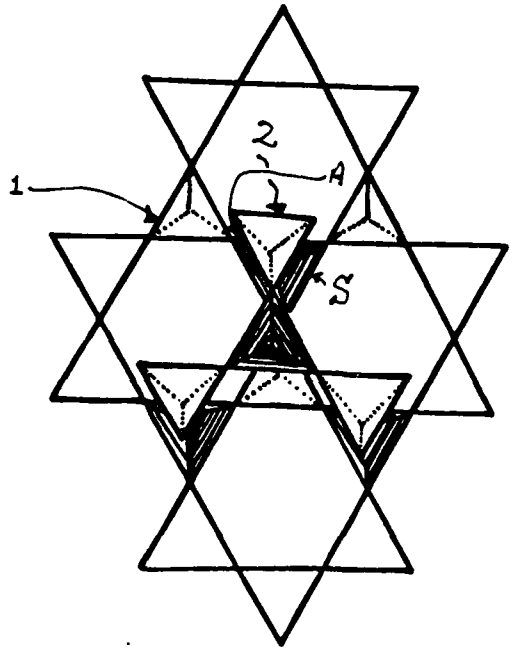

Figure 41: The first neighbors of S which are second neighbors of T. The first neighbor 2 of S which is above S and the edge A of S through which two 6-rings must pass.

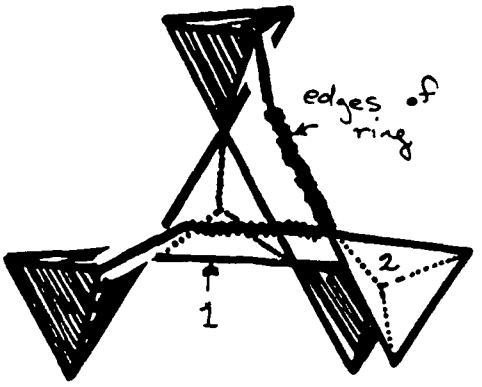

Figure 42: The two first neighbors 1 and 2 of edge A and the pair of second-neighbors through which its 6-rings must pass.

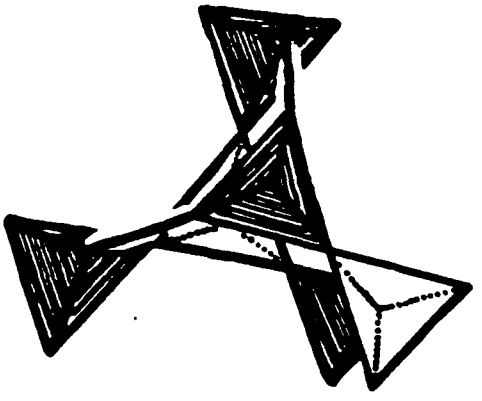

Figure 43: The arrangement of the two 6-rings through edge A. The two hatched edges belong to a first-neighbor tetrahedron of 2.

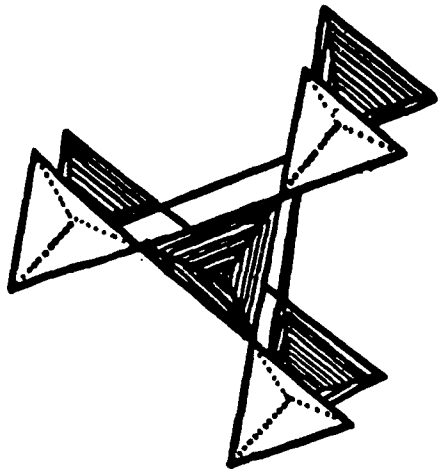

Figure 44: The tetrahedron through the hatched edges of the previous figure.

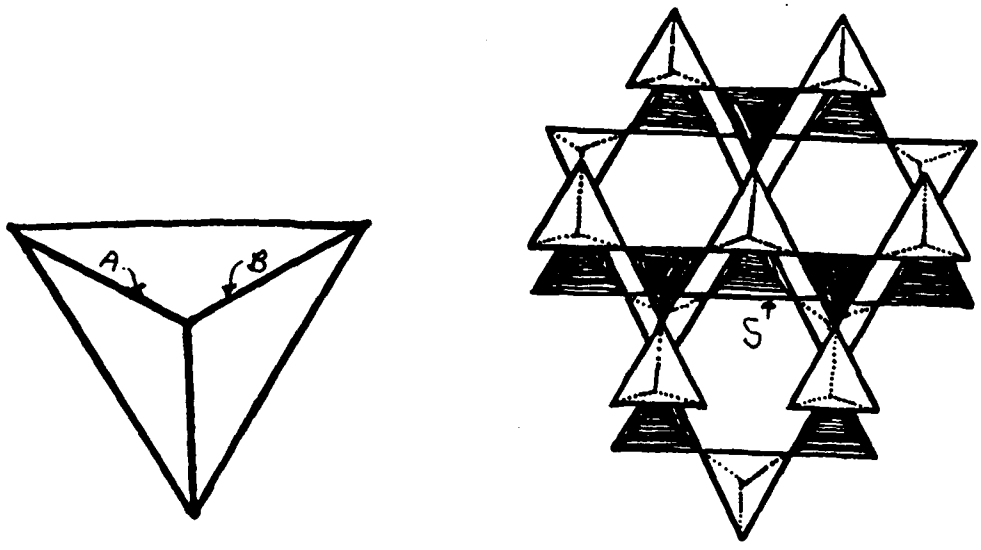

Figure 45: The tetrahedra T and S and the two edges A and B of S. The top part of the local cluster of T which is assumed to be tridymite is shown.